IV. Recent evidence for long-range transport of anthropogenic pollution

A. Recent Scientific Findings

During the past decade research accomplished by IGAC and its related international programs have discovered some essential chemistry and transport processes that control the long-range transport of short-lived chemical compounds. The aim of this section is to discuss the recent scientific findings that form the basis for future investigations.

1. Ozone from North America dominates ozone distribution in North Atlantic during the summer

Surface measurements have shown that ozone pollution from North America is easily detectable 1500 km downwind from the North American source region [Parrish et al., 1993]. Subsequently, surface measurements, located 3000 km downwind from the sources established that North American pollution enhances O_3 levels in the central North Atlantic, in the spring [Parrish et al., 1998].

These observations provided the basis for the quantitative assessment of the amount of anthropogenic O_3 transported from North America. Parrish et al. [1993] concluded that in the summer, O_3 transported from North America exceeded natural O_3 from the stratosphere in the lower troposphere over the North Atlantic. Further quantitative refinements of the calculations estimate that the total flux of ozone from North America to the North Atlantic in the summer is on the order of 1.0 to 1.6 Gmol/day [Chin et al., 1994; Berkowitz et al., 1996]. These studies conclusively show that during the summer, the O_3 budget in the lower troposphere over the temperate western North Atlantic is dominated by O_3 photochemically produced from O_3-precursors emitted by North American sources.

2. Emissions from Asia influence chemical composition over the northwest Pacific

Investigations were made of the long-range transport of atmospheric trace species over the northwest Pacific Ocean [Hoell et al., 1997]. The results have been used to estimate the magnitude of the human influence on the chemical composition of the atmosphere over the region. The region of maximum outflow lay between approximately

20˚ N and 40˚ N. The delivery of NO_x enriched from the Asian continent to the free troposphere and the subsequent redistribution by large-scale dynamics can influence the ozone production over large areas of the pacific basin [Crawford et al, 1997].

3. Oxidized sulfur over western Pacific attributed to Asian sources

Measurements were made of the chemical composition of the atmosphere over the western Pacific. These measurements [Thornton et al., 1997] indicated that in the region throughout the well-mixed troposphere the oxidized sulfur, sulfur dioxide and sulfate in aerosols were largely associated with emissions of sulfur dioxide from sources located on the Asian continent. The principal component of oxidized sulfur was sulfur dioxide. This suggests that cloud and precipitation scavenging was an effective removal mechanism for aerosol sulfate.

4. Mechanism for the transport of North America pollution to the North Atlantic

Meteorological measurements show that during the summer, inversions can effectively isolate the marine boundary layer (MBL) from the lower midtroposphere aloft, where the majority of the pollutants are transported in highly stratified layers [Angevine et al., 1996]. The processes that form these layers provide an effective mechanism for the transport of continental pollution into the mid- and upper-troposphere of the North Atlantic. In general, these processes likely play an important role in the transport of continental O_3 and O_3-precursors from the eastern coastal regions of all continents into the marine atmosphere that they border.

5. The role that fronts play in transporting continental pollution

The primary direction for transport of North American pollution to the North Atlantic in the summertime is toward the northeast. In general terms, this can be viewed as the result of the prevailing westerly winds developing a southerly component as air masses come under the influence of the clockwise circulation of the Bermuda-Azores high. However, warm sector flow ahead of advancing cold fronts has been identified as the most important process for the transport of pollution from the urbanized U.S. East Coast to the North Atlantic [Merrill and Moody, 1996; Berkowitz et al., 1996]. This

mechanism provides a means to rapidly and effectively transport large amounts of relatively short-lived pollution over long distances.

6. *The role that the oxides of nitrogen (NOx) and volatile organic compounds (VOCs) play in the O_3 budget of the North Atlantic troposphere*

In the remote, marine troposphere, the concentrations of carbon monoxide (CO) and methane (CH_4) are adequate to support significant photochemical ozone formation. However, whether this photochemistry produces rather than destroys ozone is determined by the amount of NO_x available [Fehsenfeld and Liu, 1993]. Hence, the export of pollution-produced NO_x from the continental boundary layer can determine the amount of ozone that is produced in the marine troposphere. Analysis of the correlation of NOy and its component species with CO has demonstrated that only a small fraction of the NO_x emitted in the continental boundary layer is transported to the free troposphere [Parrish et al., 2000b]. Lagrangian trajectory analyses independently show that only a limited amount of NO_x is transported from North America to the North Atlantic [Stohl et al., 2000].

Although there is limited transport of reactive nitrogen from the continent to the marine free troposphere, continental NO_x emissions are believed to still have a significant impact on ozone distribution in the remote marine troposphere. Model results suggest that eventual ozone production in the global troposphere from U.S. emissions is about twice as large as the direct export of ozone from the U.S. boundary layer [Liang et al., 1998; Horowitz et al., 1998; Meijer et al., 2000]. The amount of NO_x delivered to the lower troposphere in the western North Atlantic during summer is sufficient to produce, on average, 1 to 4 ppbv/day of ozone throughout the region [Duderstadt et al., 1998; Parrish et al., 1998]. In contrast, the central North Atlantic (e.g., the Azores) is a region of photochemical ozone destruction [Peterson et al., 1998; Atherton et al., 1996; Parrish et al., 1998].

7. *Role of aircraft emissions of NO_x relative to lightning and surface emissions in ozone formation*

Recent studies have examined the sources of the oxides of nitrogen in the remote free troposphere over the North Atlantic [Ziereis et al., 2000; Meijer et al., 2000]. The studies indicate that emissions from aircraft and lightning in the free troposphere and transport from the surface play a significant role in determining the NO_x distribution and the consequent formation of ozone in the free troposphere. These sources are found to vary with latitude: aircraft emission being relative more important at high latitudes, lightning at low latitudes.

8. Intercontinental transport of emissions from forest fires

The principal sources of CO in the Northern Hemisphere are fossil fuel combustion, biomass burning, and oxidation of methane and non-methane hydrocarbons. Recent research has focused on and elucidated the importance of boreal forest fires to northern hemispheric summertime CO background concentrations [Wotawa and Trainer, 2000]. Hemispheric background concentrations of CO declined from late 1980's through the middle of the 1990's. This decline was associated with emission control of CO in the industrial countries of the Northern Hemisphere. This trend has been perturbed since that period by a rapid increase in CO emissions associated with biomass combustion due to wild fires in the boreal regions of North America and Russia. The emission of the NO_x, combustion-produced VOCs, and carbon aerosols may also perturb the atmsopheric chemistry in the Northern Hemisphere. The increase in these forest fire emissions is the direct result of climate variability that has produced drought conditions in the boreal regions during the last ten years.

9. The seasonal variation of the anthropogenic influence on the tropospheric O_3 budget

All of the NARE summertime studies in the western North Atlantic have found a positive correlation between CO and O_3. This positive correlation demonstrates that anthropogenic pollution produces ozone in the summer, as discussed above. However, in the wintertime a negative correlation between CO and O_3 is observed, both at surface sites [Parrish, 1993] and in the free troposphere [Parrish et al., 1998; 2000a]. This negative correlation demonstrates that anthropogenic pollution provides a sink for ozone in the winter. The mechanism of this destruction is consistent with the expected reaction

of O_3 with some of the primary pollutants (e.g., NO and unsaturated VOCs). This destruction is expected to occur in all seasons. However, photochemical formation of O_3 more than compensates for the destruction in summer, but not in winter. A simple model based on O_3 correlations with CO demonstrates that the anthropogenic contribution to the O_3 budget over the western North Atlantic is positive in the summer, near zero in the spring, and likely negative in the winter [Parrish et al., 1999].

However, it has not been determined if the overall anthropogenic effect on O_3 in the winter is negative further from the continent. In winter, slow photochemical O_3 production likely occurs over longer transport times and distances in the troposphere. Long-range transport of anthropogenic precursors to low latitudes with more photochemical activity could possibly further enhance O_3 formation in the remote marine troposphere. A combination of these processes may compensate for the initial O_3 destruction. These are important questions to answer in order to gauge properly the seasonal dependence of the global climate warming potential of anthropogenic O_3.

B. Evidence for impacts

There is ample evidence for the impact of long-range transport of ozone, fine particles, and their precursors. The long-range transport of dust particles from Asia and Africa has been extensively documented [Prospero, 1979; Duce et al, 1980; Talbot et al., 1986; Prospero and Savoie, 1989; Xiao et al., 1998]. Estimations also indicate that there is an increasing trend in the mixing ratio of ozone over the Northern Hemisphere [c.f., Marenco, et al., 1994] that is probably associated with anthropogenic influences on the chemical composition of the atmosphere.

More specifically, several reports have recently appeared in the published literature documenting events that give clear evidence for intercontinental transport of ozone, ozone precursors, and other chemical compounds. In general, these events are limited to the spring and fall season in the Northern Hemisphere when zonal flow from west to east is stronger and chemical processing and vertical mixing in the atmosphere are less.

Measurements made from island locations in the Atlantic and Pacific have recorded events of increased concentrations of ozone and carbon monoxide. Measurements [Jaffe et al, 1998a] made at Shemya, Alaska indicate that in the spring and fall there are periods

of enhanced CO and O_3 concentrations that were attributable to long-range transport of pollution from Asia. Enhancements in CO attributable to Asian sources have been observed in Shemya, Guam, Midway, and Hawaii [Jaffe et al, 1998b]. Likewise, enhanced concentrations of ozone and carbon monoxide attributable to anthropogenic sources in North America have been observed in the Azores [Parrish et al., 1998] during the spring.

Measurements made during the spring on the West Coast of the United States have detected Asian influence on the levels of several atmospheric species. In 1985 Parrish et al. [1992] found that levels of O_3, peroxyacetyl nitrate (PAN), nitric acid (HNO_3) and the light alkanes were enhanced during periods when trajectory analysis indicated rapid transport from Asia. Effective lifetimes of O_3 and PAN in the marine troposphere were derived from the correlation of the levels of these compounds with the ratios of the alkanes. In 1997 Jaffe et al. [1999] detected enhanced concentrations of CO and PAN that could be identified as byproducts of emissions from the Asian continent. The enhancements in ozone concentrations during these episodes were too small to be reliably extracted from the background ozone concentrations. However, model simulations undertaken as part of the study reproduced the observed enhancements in CO and PAN, and indicated that the ozone over the western United States was also enhanced. Other model simulations [Jacob et al., 1999] appear to support this conclusion and, also, indicate that significant enhancements in the average ozone concentration over the Western United States might occur if Asian emissions of ozone precursors are significantly increased.

Elevated concentrations of ozone that are attributed to long-range transport from the boundary layer over North America were observed over Europe [Stohl and Trickl, 1999] during an event that occurred in the spring of 1997. Ozone mixing ratios as high as 100 ppbv were measured in the free troposphere. The high concentrations recorded during this episode were explained by the effective transport without significant dilution of boundary layer air that was carried by an ascending air stream at the leading edge of a trough.

Clearly numerous aspects of long-range transport have been widely investigated. What is missing is a systematic and quantitative understanding of the budgets of the

important trace species on a hemispheric to global scale. This is particularly true for the O_3 budget; there is as yet no agreement on the relative importance of natural and anthropogenic sources of ozone to the Northern Hemisphere troposphere. One of the major tasks facing ITCT is to provide this quantitative analysis.